Claims

We claim:

1. A method of fragmenting ions, comprising:

a) trapping ions in an ion trap, the trap being disposed in an environment in which a background gas is present at a pressure of less than approximately 9×10^{-5} Torr; and

b) resonantly exciting selected trapped ions for an excitation period exceeding approximately 25 milliseconds, to thereby promote collision-induced dissociation of at least a portion of the trapped ions.

2. A method according to claim 1, wherein the selected trapped ions are resonantly excited by subjecting them to an alternating potential that has a maximum amplitude of less than approximately 1 $\mathrm{volt}_{(0\text{-}pk)}$.

3. A method according to claim 1, wherein the pressure is in the range of approximately 1×10^{-5} Torr and approximately 9×10^{-5} Torr.

4. A method according to claim 2, wherein the alternating potential has a maximum amplitude of 500 $\mathrm{mV}_{(0\text{-}pk)}$.

5. A method according to claim 4, wherein the amplitude of the auxiliary alternating potential is approximately 25 $\mathrm{mV}_{(0\text{-}pk)}$.

6. A method according to claim 1, wherein the excitation period is in the range of approximately 50 milliseconds to approximately 2000 milliseconds.

7. A method according to claim 6, wherein the excitation period is in the range of approximately 50 to 500 milliseconds.

8. A method according to claim 1, wherein the selected trapped ions are resonantly excited by subjecting them to an alternating potential that has a frequency component substantially equal to a fundamental resonant frequency of a selected ion, the maximum amplitude of said component being less than approximately 1 $V_{(0\text{-}pk)}$.

9. A method according to claim 8, wherein the background gas pressure is in the range of approximately 1 x 10^{-5} Torr and approximately 9 x 10^{-5} Torr.

10. A method according to claim 8, wherein the excitation period is in the range of approximately 50 milliseconds to approximately 2000 milliseconds.

11. A method according to claim 10, wherein the excitation period is in the range of approximately 50 to approximately 500 milliseconds.

12. A method according to claim 9, wherein the amplitude of said component is in the range of approximately 10 $mV_{(0\text{-}pk)}$ to approximately 500 $mV_{(0\text{-}pk)}$.

13. A method according to claim 12, wherein the amplitude of said component is approximately 25 $mV_{(0\text{-}pk)}$.

14. A method according to any of claims 1, 2, 3, 4, 6 and 8, wherein the ion trap provides a non-ideal quadrupolar field for trapping ions.

15. A method of fragmenting ions, comprising:

c) trapping ions in an ion trap by subjecting the ions to an RF alternating potential, the trap being disposed in an environment in which a background gas is present at a pressure of less than approximately 9 x 10^{-5} Torr;

d) resonantly exciting trapped ions of a selected m/z value or valves by applying to at least one set of poles straddling the trapped ions an auxiliary alternating excitation signal for a period exceeding approximately 25 milliseconds, to thereby promote collision-induced dissociation of the selected ions.

16. A method according to claim 14, wherein the excitation signal has an amplitude of less than approximately $1V_{(0\text{-}pk)}$.

17. A method according to claim 16, wherein the ion trap includes one or more poles that have non-hyperbolic cross-sections.

18. A method according to claim 17, wherein said poles have substantially circular cross-sections.

19. A method according to claim 16, wherein the excitation signal has a frequency substantially equal to a fundamental resonant frequency of the selected ions or a harmonic thereof.

20. A method according to claim 17, wherein the frequency of the excitation signal is varied through a pre-determined range encompassing the fundamental resonant frequency of the selected ions or a harmonic thereof.

21. A method according to claim 16, wherein the ion trap is a linear ion trap comprising two pole sets, the excitation signal being applied to only one pole set.

22. A method according to claim 20, wherein the background gas pressure is on the order of 10^{-5} Torr.

23. A method according to claim 22, wherein the amplitude of the excitation signal is in the range of approximately $10\ mV_{(0\text{-}pk)}$ to approximately $500\ mV_{(0\text{-}pk)}$.

24. A method according to claim 23, wherein the excitation period is in the range of approximately 50 to 2000 milliseconds.

25. A method according to claim 23, wherein the frequency of the excitation signal is varied through a pre-determined range encompassing the fundamental resonant frequency of the selected ions or a harmonic thereof

26. A method according to claim 16, wherein the ion trap is a linear ion trap comprising two pole sets, the excitation signal being applied to both pole sets.

27. A method according to claim 26, wherein the background gas pressure is on the order of 10^{-5} Torr.

28. A method according to claim 27, wherein the amplitude of the excitation signal is in the range of approximately 10 $mV_{(0\text{-}pk)}$ to approximately 500 $mV_{(0\text{-}pk)}$.

29. A method according to claim 28, wherein the excitation period is in the range of approximately 50 to 2000 milliseconds.

30. A method according to claim 23, wherein the frequency of the excitation signal is varied through a pre-determined range encompassing the fundamental resonant frequency of the selected ions or a harmonic thereof.

31. A method according to claim 16, including mass analyzing the fragmented ions to obtain a mass spectrum.

32. A method of mass analyzing a stream of ions, the method comprising:

a) subjecting a stream of ions to a first mass filter step, to select precursor ions having a mass-to-charge ratio in a first desired range;

b) trapping the precursor ions in a linear ion trap by subjecting the ions to an RF alternating potential;

c) resonantly exciting selected trapped precursor ions by subjecting them to an auxiliary alternating potential having a maximum amplitude of less than approximately $1V_{(0\text{-}pk)}$ for an excitation period exceeding approximately 50

milliseconds under a background gas pressure of less than 9×10^{-5} Torr, to thereby generate fragment ions; and

d) mass analyzing the trapped ions to generate a mass spectrum.

33. A method according to claim 32, wherein the linear ion trap includes one or more poles that are non-hyperbolic in cross-section.

34. A method according to claim 32, including, before step (d):

a) subjecting the trapped ions to a second mass filter step in order to isolate ions having an m/z value(s) in a second desired range, and

b) repeating step (c).

35. A method according to claim 32, wherein the pressure is on the order of 10^{-5} Torr.

36. A method according to claim 32, wherein the excitation period is in the range of approximately 50 to approximately 2000 milliseconds.

37. A method according to claim 32, wherein the amplitude of the auxiliary alternating potential is in the range of approximately 10 $mV_{(0\text{-}pk)}$ to approximately 500 $mV_{(0\text{-}pk)}$.

38. A method of mass analyzing a stream of ions, the method comprising:

a) subjecting a stream of ions to a first mass filter step, to select precursor ions having a mass-to-charge ratio in a first desired range;

b) fragmenting the precursor ions in a collision cell, to thereby produce a first generation of fragment ions;

c) trapping any un-dissociated precursor ions and the first generation of fragment ions in a linear ion trap by subjecting the ions to an RF alternating potential, and:

(i) subjecting the trapped ions to a second mass filter step, to thereby isolate ions having an m/z value(s) in a second desired range,

(ii) resonantly exciting selected first generation ions by subjecting them to an auxiliary alternating potential for an excitation period exceeding approximately 25 milliseconds under a background gas pressure of less than about 9×10^{-5} Torr, to thereby generate a second generation of fragment ions, and

d) mass analyzing the trapped ions to generate a mass spectrum.

39. A method according to claim 38, wherein the alternating potential has a maximum amplitude of approximately $1V_{(0\text{-}pk)}$.

40. A method according to claim 38, wherein the linear ion trap includes one or more poles for applying the alternating potential that are non-hyperbolic in cross-section.

41. A method according to claim 38, including repeating steps (c)(i) and (c)(ii) to thereby generate subsequent generations of fragment ions.

42. A method according to claim 38, wherein the pressure is on the order of 10^{-5} Torr.

43. A method according to claim 38, wherein the excitation period is in the range of approximately 50 to approximately 2000 milliseconds.

44. A method according to claim 39, wherein the amplitude of the auxiliary alternating potential is in the range of approximately 10 $mV_{(0\text{-}pk)}$ to approximately 500 $mV_{(0\text{-}pk)}$.

45. A method of mass analyzing a stream of ions, the method comprising:

a) subjecting a stream of ions to a first mass filter step, to select precursor ions having a mass-to-charge ratio in a first desired range;

b) fragmenting the precursor ions in a collision cell, to thereby produce a first generation of fragment ions;

c) trapping any un-dissociated precursor ions and the first generation of fragment ions in a linear ion trap, and:

(i) subjecting the trapped ions to a second mass filter step, to thereby isolate ions having an m/z value(s) in a second desired range,

(ii) resonantly exciting trapped ions of a selected m/z value or values by applying to at least one set of poles straddling the trapped ions an alternating excitation signal for a period exceeding approximately 25 milliseconds, to thereby promote collision-induced dissociation of the selected ions, and

d) mass analyzing the trapped ions to generate a mass spectrum.

46. A method according to claim 45, wherein the excitation signal has an amplitude of less than approximately $1V_{(0\text{-}pk)}$

47. A method according to claim 45, wherein excitation signal is applied to poles that have non-hyperbolic cross-sections.

48. A mass spectrometer, comprising:

a linear ion trap, including at least one set of poles straddling at least a portion of trapped ions;

means for providing a background gas in said trap at a pressure of less than approximately 9×10^{-5} Torr;

means for introducing ions into said trap;

an alternating voltage source for applying to said at least one of set of poles a resonant excitation signal for a period exceeding approximately 25 milliseconds in order to promote collision-induced dissociation of selected ions; and

means for mass analyzing the trapped ions to generate a mass spectrum.

49. A mass spectrometer according to claim 48, wherein the resonant excitation signal has an amplitude of less than approximately $1V_{(0\text{-}pk)}$.

50. A mass spectrometer according to claim 48, wherein each of said at least one pair of poles have non-hyperbolic profiles.

51. A mass spectrometer according to claim 50, wherein said at least one set of poles is not used to trap said ions in said trap.

52. A triple quadrupole mass spectrometer, comprising:

first, second and third quadrupole rod sets arranged in sequence;

said first quadrupole rod set being configured for isolating selected ions;

said second quadrupole rod set being enclosed within a collision chamber having a background gas pressure significantly higher than the first and second rod sets;

said third quadrupole rod set being configured as a linear ion trap, including at least one set of poles straddling at least a portion of trapped ions, the trap having a background gas pressure of less than approximately 9×10^{-5} Torr;

an alternating voltage source for applying to said at least one set of poles a resonant excitation signal having an amplitude of less than approximately $1V_{(0\text{-}pk)}$ for a period exceeding approximately 25 milliseconds in order to promote collision-induced dissociation of selected ions; and

means for mass analyzing the trapped ions to generate a mass spectrum.

53. A mass spectrometer according to claim 52, wherein said at least one set of poles is not used to trap said ions in said third quadrople rod set.

54. The mass spectrometer according to claim 52, wherein the third quadrupole rod set has poles that each have a non-hyperbolic cross-sectional profile.